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(54) PHOTOREACTIVE COMPOSITION, ACID-REACTIVE HIGH POLYMER COMPOSITION CONTAINING THE SAME AND ACID-REACTIVE RESIN LAYER

(57)Abstract:
PURPOSE: To obtain a photoreactive composition having improved photosensing speed through amplifying photochemical reaction by using as the components of the composition, a photo-acid-generating agent that generates acid with the effect of light and an acid-breeding agent that newly generates acid with the acid generated by the photo-acid-generating agent.
CONSTITUTION: This composition consists of a photo-acid-generating agent that generates acid with the effect of light and an acid-breeding agent that newly generates acid with the acid generated by the photo-acid-generating agent. Namely, by using a combination of the acid-breeding agent that newly generates acid with the catalytic effect of acid and the photo- acid generating agent, for example, one acid molecule is generated and, one molecule of the acid-breeding agent is decomposed by one acid molecule generated with the photo-acid- generating agent into newly formed one or more acid molecules and therefore, the one or more acid molecules are bred into two or more acid molecules by each acid-catalytic reaction and thus, these reactions are caused in a chainlike manner to increase the acid molecules in a geometrical-progressional manner. By adding the acid-breeding agent having such characteristics, the amount of acid is rapidly increased and as a result, termination of the acid-catalytic reaction due to any basic substance and disappearance of the acid by any side reaction can be prevented from occurring and thereby, the acid-catalytic reaction can be accelerated.

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CLAIMS

[Claim(s)]
[Claim 1] The photoreaction nature constituent which consists of a photo-oxide generating agent which generates an acid according to an operation of light, and an acid growth agent which newly generates an acid with the acid generated from this photo-oxide generating agent.
[Claim 2] The acid reactive polymer constituent characterized by making the photo-oxide generating agent which generates an acid according to an operation of light, and the acid growth agent which newly generates an acid according to an operation of this acid exist in the high polymer which mixed the matter which produces molecular structure change according to an operation of an acid, or the high polymer which combined the residue which produces molecular structure change according to an operation of an acid.
[Claim 3] The high polymer which mixed the matter which produces molecular structure change according to an operation of an acid, Or the acid growth agent which newly generates an acid with the acid generated from said photo-oxide generating agent in the resin layer which consists of a high polymer which combined the residue which produces molecular structure change according to an operation of an acid, and a photo-oxide generating agent, The acid reactivity resin layer which has the two-layer structure which carried out the laminating of the different resin layer from the aforementioned resin layer which consists of a high polymer which mixed the matter which produces molecular structure change according to an operation of the newly generated acid, or a high polymer which combined the residue which produces molecular structure change according to an operation of an acid.

[Translation done.]

DETAILED DESCRIPTION

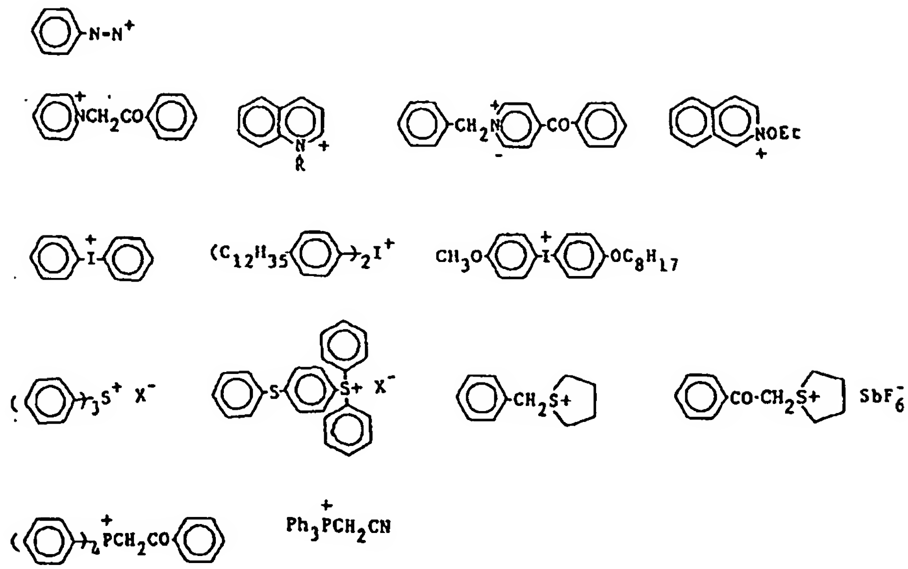
[Detailed Description of the Invention]
[0001]
[Industrial Application] This invention relates to the acid reactive polymer constituent and acid reactivity resin layer containing this photoreaction constituent further about the photoreaction constituent which raised the sensitization rate by combining the matter (it being hereafter called an acid growth agent) which newly generates an acid with the generated acid with the matter (it being hereafter called a photo-oxide generating agent) which generates an acid in an operation of light.
[0002]
[Description of the Prior Art] Light energy is absorbed conventionally and it is used in the direction chemical between intramolecular or a molecule or of versatility [ingredient / which has the photosensitive function which produces a physical change]. For example, in many fields, it is used and using as an image formation ingredient which detects optically the chemical structural change produced by the photoreaction, or using as a surface coating processing ingredient which performs surface treatment by the photo-curing of a monomer or a prepolymer etc. is put in practical use. However, the sensitization rate in the ingredient which has these photosensitive functions, a sensitization wavelength field, and definition are various, and the ingredient which has a suitable property according to the purpose is chosen.
[0003] Although silver salt sensitive material was used more widely in ancient times as an ingredient which has a photosensitive function, the photopolymer which uses polymeric materials as a principal component reaches far and wide as extensive and the high sensitivity image formation ingredient in which high definition is shown, and it came (refer to the volume Yamaoka Tsugio and for Gentaro Matsunaga, "photopolymer technology", and Nikkan Kogyo Shimbun (1988)) to be used in recent years. [as / in a photoengraving-process technique etc.] The macromolecule system photosensitivity ingredient is not only excellent in definition, but can set up a wide range sensitization wavelength field by selection of the photoreaction. Moreover, it has many advantages of being able to manufacture comparatively cheaply. However, a sensitization rate is very low in comparing with a silver salt photosensitivity ingredient, and also although it is called the high sensitivity macromolecule system photosensitivity ingredient, the present condition is not amounting to 1/1000 of the sensitization rate which a silver salt ingredient's shows.
[0004] In order to raise the sensitization rate of a macromolecule system photosensitivity ingredient, various attempts have so far been made. It is the photopolymerization system to which having been most widely set as the object of development carries out the polymerization of many vinyl monomers continuously by making into an initiator the radical kind generated in an operation of light. However, since the oxygen in air and the radical kind which reacts easily are growth kinds, it ends, without completing sufficient chain reaction. Moreover, with advance of a radical polymerization reaction, diffusion of a monomer is quickly controlled for the network structure within the macromolecule matrix formed rapidly, and a polymerization cannot be completed. For such a cause, essential threshold value exists in the sensitization rate of a photopolymerization system.

[0005] Creation of various macromolecule system photosensitivity ingredients was attained by generating an acid in an operation of light and on the other hand, combining not only the cationic polymerization that makes this acid a catalyst but various acid catalyzed reactions. Although high sensitivity is expected since there is no halt effectiveness of the reaction by oxygen unlike a radical polymerization, the sensitization rate of the present condition is rather lower in cationic polymerization, than a radical polymerization system in fact for the moisture in air, or network structure formation. Moreover, let it be a principle to heat-treat, after generating an acid with light, and to carry out induction of the acid catalyzed reaction with the macromolecule system photosensitivity ingredient incorporating an acid catalyzed reaction. For this reason, this kind that makes a photoresist a main use gestalt of giant-molecule system photosensitivity ingredient is called the chemistry magnification mold photoresist. However, the present condition is that a sensitization rate is less than a radical polymerization system, and improvement in a fast sensitization rate has still been called for.
[0006] Furthermore, by using an optical radical polymerization and optical cationic polymerization, or combining the both, the resin constituent which hardens a film-like resin coat to a high degree of hardness by optical exposure is also large liquefied, and practical use is presented. Although the optical cationic polymerization system which does not receive the inhibition effectiveness by the oxygen in air is widely set as the object of development research and development of the monomer and prepolymer suitable for the photo-oxide generating agent suitable for hardening or hardening is performed actively in recent years, improvement in a cure rate is called for for speeding up of a hardening process. Furthermore, since hardening of the resin constituent and the thick coat which the pigment which absorbs light distributed takes place only by the surface layer, the essential trouble that sufficient hardening is not brought about has resulted as it is not solved. Moreover, it thinks for the base component of the minute amount which floats in air to bring about a poisoning operation of a catalyst as a cause by which it will not become so high although the sensitization rate of the above-mentioned chemistry magnification mold photoresist uses the acid catalyzed reaction, or the acid catalyzed reaction in the inside of a macromolecule matrix triggers side reaction, and it is also considered that an acid catalyzed reaction stops for this reason.
[0007]
[Problem(s) to be Solved by the Invention] The result to which this invention person examined various the approaches of solving such a situation radically, It is what completed a header and this invention for the photoreaction constituent which raised the sensitization rate remarkably by combining the matter which newly generates an acid with the generated acid with the matter which generates an acid in an operation of light. The purpose of this invention offers the photoreaction constituent which was made to amplify photochemical reaction and raised the sensitization rate remarkably.
[0008]
[Means for Solving the Problem] The photo-oxide generating agent in which the summary of invention of the 1st of this application generates an acid according to an operation of light, It is the photoreaction nature constituent which consists of an acid growth agent which newly generates an acid with the acid generated from this photo-oxide generating agent. The photo-oxide generating agent which generates an acid according to an operation of light in the high polymer which mixed the matter from which the summary of the 2nd invention produces molecular structure change according to an operation of an acid, or the high polymer which combined the residue which produces molecular structure change according to an operation of an acid, It is the acid reactive polymer constituent characterized by making the acid growth agent which newly generates an acid according to an operation of this acid exist. The high polymer which mixed the matter from which the summary of the 3rd invention produces molecular structure change according to an operation of an acid, Or the acid growth agent which newly generates an acid with the acid generated from said photo-oxide generating agent in the resin layer which consists of a high polymer which combined the residue which produces molecular structure change according to an operation of an acid, and a photo-oxide generating agent, The aforementioned resin layer which consists of a high polymer which mixed the matter

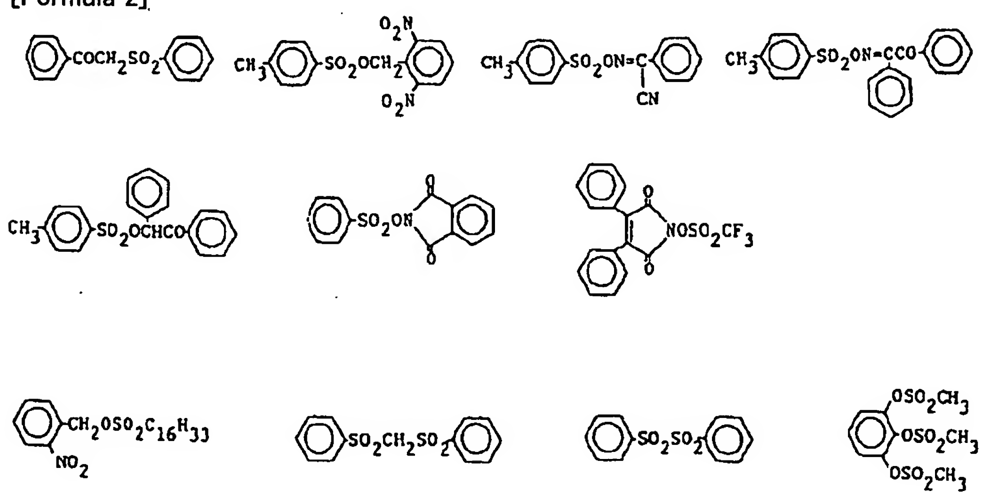
which produces molecular structure change according to an operation of the newly generated acid, or a high polymer which combined the residue which produces molecular structure change according to an operation of an acid is an acid reactivity resin layer which has the two-layer structure which carried out the laminating of the different resin layer. Namely, by combining with a photo-oxide generating agent the acid growth agent which newly generates an acid according to an operation of an acid in this invention Since one acid is generated, and this acid disassembles an acid growth agent molecule and newly generates one or more acids from a photo-oxide generating agent according to an operation of light One or more acid-content children will increase at one reaction, it will become a total of two or more acid-content children, this reaction will arise continuously, and generating of an acid will increase in multiplying like rats. That is, by addition, an acid can also prevent a halt of the acid catalyzed reaction by increase, consequently the alkali rapidly, and disappearance of the acid by side reaction can also prevent an acid growth agent with such a property, and an acid catalyzed reaction can be accelerated sharply. It is as follows when the principle of an above-mentioned reaction principle is illustrated.

$AG \longrightarrow H^{+}$ ……………… 光酸発生
$\downarrow$
$m \times X \longrightarrow m \times H^{+}$ ……………… 酸増殖反応
$\downarrow$
$n \times M \longrightarrow n \times N$ ……… 酸触媒反応

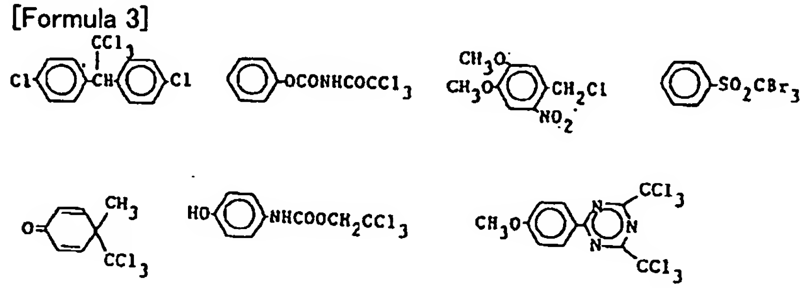
AG Photo-oxide generating agent; X Acid growth agent;M Acidolysis product; N The acidolysis products m and n are molecularity. The organic compound which increases such an acid was used, and the growth reaction which generates an acid in multiplying like rats was not known at all as an organic chemistry reaction until now, although it was similar to a nuclear fission reaction or explosive reaction. Although it is thermally stable as much as possible, an acid decomposes and an acid growth agent generates strong acid itself, it is the compound permuted by the residue of a comparatively strong acid, and triggers an elimination reaction comparatively easily and generates an acid. Therefore, although it is stable under un-existing [of an acid] if this elimination reaction can be sharply activated by the acid catalyzed reaction, under existence of an acid, it becomes possible to make thermal reaction generate an acid easily. By combining an acid growth agent with such a property with a photo-oxide generating agent, the photosensitive ingredient whose sensitization rate improved by leaps and bounds became possible.
[0009] This invention is explained to a detail. As a photo-oxide generating agent which generates an acid according to an operation of light in this invention, the compound used for a chemistry magnification mold photoresist or optical cationic polymerization is used (the volume on organic electronics ingredient study group, "imaging business refer to organic material", the **** exudation version (1993), and 187 - 192 pages). The example of the suitable compound for this invention is given to below. Moreover, in order to expand the sensitization wavelength field of these photo-oxide generating agents, a photosensitizer can also be made to live together suitably. With the acid active substance, the acid generated by the photolysis of these matter acts on an acid growth agent, and promotes generating of an acid. The following photo-oxide generating agents can be used. PF6- of aromatic series onium compounds, such as diazonium, ammonium, iodonium, sulfonium, and phosphonium, AsF6-, SbF6-, and a CF3SO3-salt can be mentioned [1st]. The concrete example of an onium compound is shown below.
[0010]
[Formula 1]



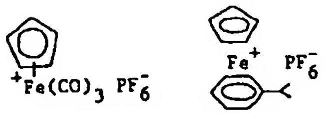
[0011] The sulfonation object which generates [2nd] a sulfonic acid can be mentioned. A concrete compound is illustrated below.
[0012]
[Formula 2]



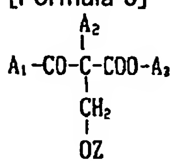
[0013] The halogenide which carries out optical generating of the hydrogen halide can also be used [3rd]. A concrete compound is illustrated below.
[0014]
[Formula 3]



[0015] An iron allene complex can be mentioned to the 4th.
[0016]
[Formula 4]

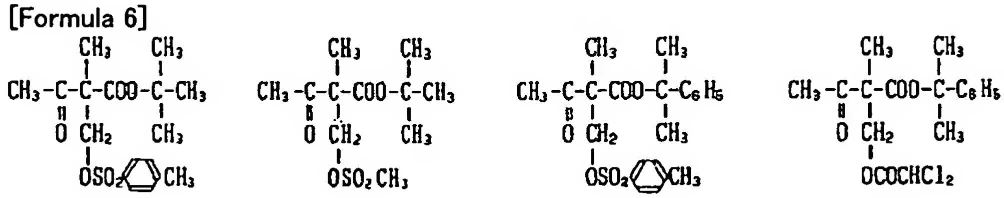


[0017] The acid growth agent used by this invention is the compound permuted by the residue of a comparatively strong acid, and is a compound which triggers an elimination reaction comparatively easily and generates an acid. Therefore, this elimination reaction can be sharply activated by the acid catalyzed reaction, and although it is stable under un-existing [of an acid], under existence of an acid, it becomes possible to make thermal reaction generate an acid easily. By combining an acid growth agent with such a property with a photo-oxide generating agent, the photoreaction nature constituent whose sensitization rate improved by leaps and bounds became possible. An acid catalyzed reaction decomposes and an acid (it is ZOH at the following general formulas) is generated again. One or more acids are increasing in number at one reaction, and a reaction progresses accelarative with advance of a reaction. In order for the generated acid itself to carry out induction of the autolysis, reinforcement of the acid generated here is set to an acid dissociation constant and electric dissociation exponent, and is three or less, and it is desirable that it is two especially or less. An autolysis cannot be caused if it is an acid weaker than this. As such an acid, dichloroacetic acid, a trichloroacetic acid, methansulfonic acid, ethane sulfonic acid, benzenesulfonic acid, p-toluenesulfonic acid, a naphthalene sulfonic acid, triphenyl phosphonic acid, etc. can be raised. Specifically, the following compounds can be illustrated. The organic-acid ester compound expressed [1st] with a general formula (1) can be mentioned.
[0018]
[Formula 5]

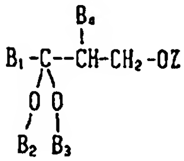


(1)

[0019] (A1 shows the alkyl group or aryl group from C1 to C6 among a formula, A2 shows the alkyl group from C1 to C6, and A3 is screw (p-alkoxy phenyl) methyl) A radical, a 2-alkyl-2-propyl group, a 2-aryl-2-propyl group, a cyclohexyl radical, or a tetrahydropyranyl group is shown, and Z shows the residue of the acid shown by ZOH whose acid dissociation constant (electric dissociation exponent) is three or less.
If an acid acts on this compound, an ester group decomposes and it becomes a carboxylic acid, and after this raises a decarboxylic acid further, an acid (ZOH) will **** easily. Specifically, an example is shown below.
[0020]
[Formula 6]

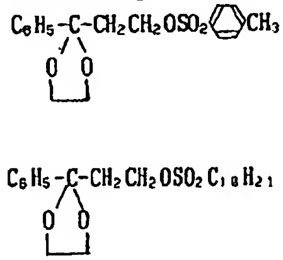


[0021] Organic-acid ester with the acetal or ketal radical expressed [2nd] with a general formula (2) can be mentioned.
[0022]
[Formula 7]

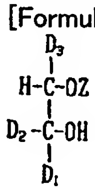


(2)

[0023] (Z has the same semantics as the above among a formula, B1 is a hydrogen atom, an alkyl group, or an aryl group, B-2 and B3 form ethylene or a propylene radical in methyl, an ethyl group, or both, and B4 shows a hydrogen atom or a methyl group)
An acetal or ketal decomposes in an operation of an acid, this compound serves as beta-aldehyde or a ketone, and ZOH is easily desorbed from it after this. A concrete example is shown below.
[0024]
[Formula 8]

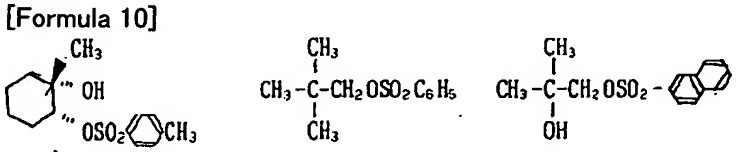


[0025] The organic-acid ester expressed [3rd] with a general formula (3) can be mentioned.
[0026]
[Formula 9]

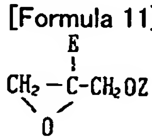


(3)

[0027] (Z has the same semantics as the above among a formula, D1 and D2 show a hydrogen atom, the alkyl groups from C1 to C6, or an aryl group, and D2 and D3 show the alkylene or permutation alkylene residue which forms alicycle-like structure on the alkyl group or both sides from C1 to C6)
After a hydroxyl group ****s, and this compound forms carbocation and carries out hydrogen migration according to an acid catalyst, it is presumed to be what ZOH generates. A concrete example is shown below.
[0028]
[Formula 10]

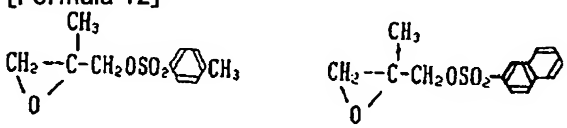


[0029] The organic-acid ester which has the epoxy ring expressed [4th] with a general formula (4) can be mentioned.
[0030]
[Formula 11]

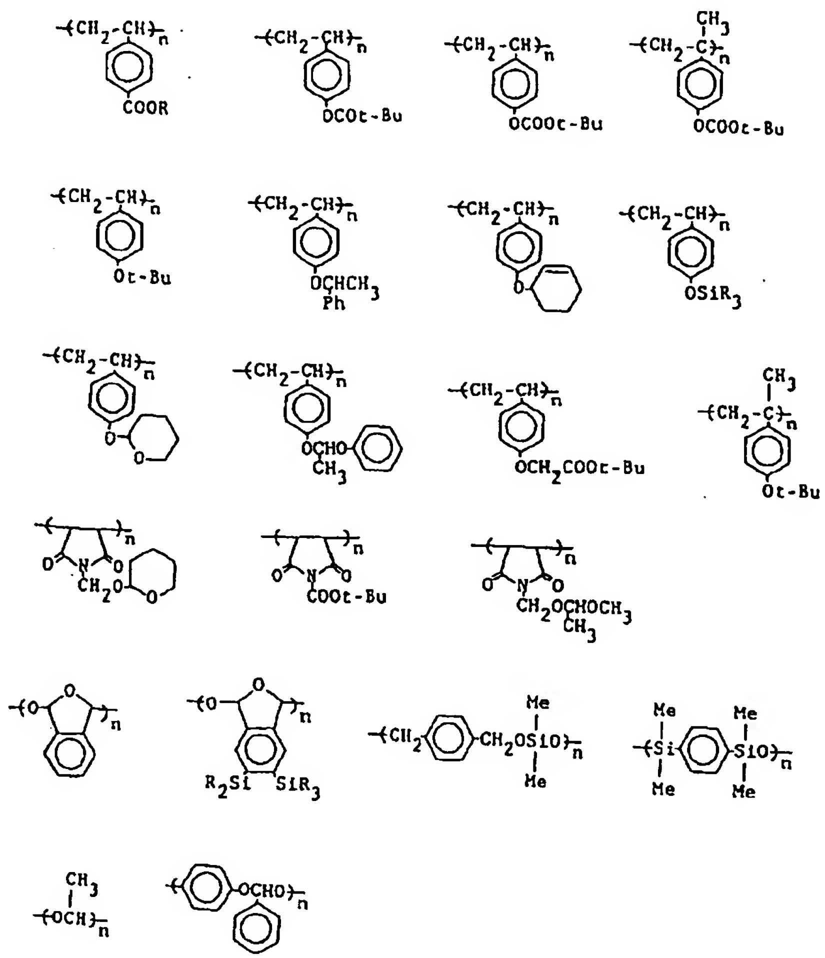


(4)

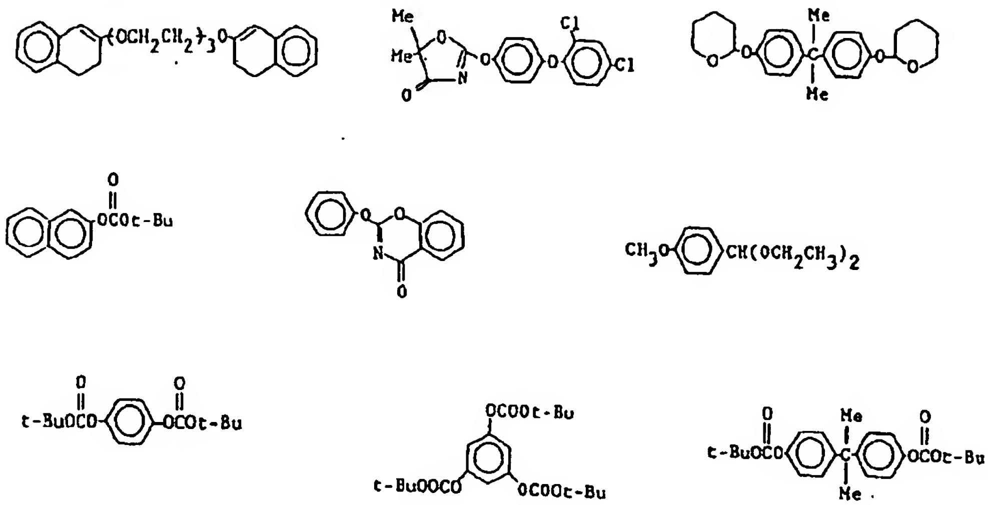
[0031] (Z has the same semantics as the above among a formula, and E shows the alkyl groups

or phenyl groups from C1 to C6)
If an acid acts on this compound, a cation will be formed in beta-carbon with generation of the ring breakage of an epoxy ring, and what an organic acid generates as a result of hydrogen migration will be presumed. A concrete example is shown below.
[0032]
[Formula 12]


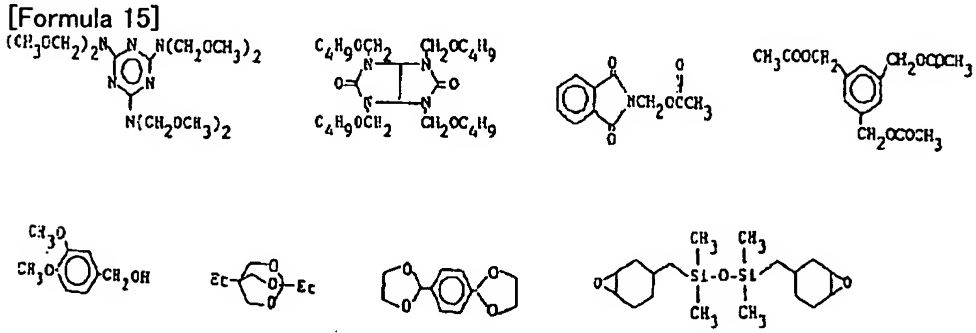
[0033] These compounds exist in stability at a room temperature, unless an acid acts. Although the acid strength more than fixed is needed in order to cause acid-catalyst disassembly of these compounds, it is desirable that it is about two or less in an acid dissociation constant pka. If it is the acid dissociation constant beyond this, i.e., a weaker acid than this, the reaction of an acid growth agent cannot be triggered.
[0034] Next, the high polymer which mixed the matter (acid reactivity molecule) which produces molecular structure change according to an operation of the acid in which the above-mentioned photoreaction constituent is made to exist, or the high polymer which combined the residue which produces molecular structure change according to an operation of an acid is explained. In addition, the matter or residue which produces molecular structure change is only called an acid reactivity molecule or acid reactivity residue. The example of a polymeric material which mixes, or joins together and becomes about the acid reactivity molecule used suitable for this invention is shown (the volume on organic electronics ingredient study group, "imaging business refer to organic material", the **** exudation version (1993), and 199 - 201 pages). many use the reaction of the deprotection radical in synthetic organic chemistry -- **** (T. refer to W.Greene, Protective Groups in Organic Synthesis, and John Wiley & Sons (1981)) -- a concrete example is shown below. The high polymer which has acid reactivity residue in a side chain or a principal chain can be mentioned to the 1st. As acid reactivity residue, the phenol nature or N-methylol nature hydroxyl group protected by the 2nd class, the 3rd class ester, the tetrahydropyranyl ester, the 3rd class ester of carbonic acid, trialkylsilyl group, and tetrahydropyranyl group of a carboxylic acid is used suitably. Since a deprotection reaction occurs and a polar high carboxylic acid and a polar high phenol generate these according to an operation of an acid, the exposure section is solubilized in a polar solvent or an alkali water solution. High sensitivity sensitive material is one of things using such a property. As an example of a concrete compound, it is [0035].
[Formula 13]



[0036] The high molecular compound containing an acid reactivity low molecular weight compound is in the 2nd. Here, an acid reactivity low molecular weight compound has the effectiveness of reducing the solubility of a resin compound, and is called a dissolution inhibitor. As a dissolution inhibitor, phenols, a pinacol derivative, etc. which were protected by an acetal compound, a ketal compound, the 3rd class ester of a carboxylic acid, tetrahydropyranyl ester, the 3rd class ester of carbonic acid, the trialkylsilyl group, or the tetrahydropyranyl group can be mentioned. As a resin compound containing these dissolution inhibitors, novolak resin, Pori (p-hydroxystyrene), a methacrylic-acid copolymer, N-methylol maleimide copolymer, etc. can be raised. Although a low molecular weight compound has the effectiveness which checks the solubility over the alkali water solution of these resin, by decomposing in an operation of an acid, this dissolution depressor effect is lost and a macromolecule serves as alkali solubilization. A concrete dissolution inhibitor is illustrated below.
[0037]
[Formula 14]



[0038] The condensation reaction by the acid catalyzed reaction is used [3rd] for the crosslinking reaction of a macromolecule. As residue which forms a cation and causes a condensation reaction by the acid catalyst, a benzyl alcohol derivative, a melamine derivative, N-methylol imide derivative, an acetal derivative, a vinyl ether derivative, etc. can be raised. Moreover, as generated KAOCHIN and residue which reacts, a phenol, alcohol, etc. can be mentioned and polymer ** of the giant molecule which has such residue, for example, the polymer of p-hydroxystyrene, novolak resin, and hydroxyethyl methacrylate is used suitably. The compound which causes a condensation reaction is illustrated below.
[0039]
[Formula 15]



[0040] Moreover, since the macromolecule having this condensation nature residue and phenyl residue causes bridge formation by the acid catalyst by itself, it is convenient for this invention. A macromolecule with the residue which carries out [4th] a polymerization according to an acid catalyst is used. As cationic polymerization nature residue, an epoxy group, oxetane residue, a vinyl ether radical, an isopropenyl phenyl group, annular orthochromatic ester, etc. can be raised. The constituent set to the 5th from a cationic polymerization nature monomer or a prepolymer is also used. As a cationic monomeric unit, an epoxy group, an oxetane radical, a vinyl ether radical, and annular orthochromatic ester are used. It is desirable to mix with a vinyl system polymer and to use these monomers or prepolymers as a free-standing filmy material.
[0041] Subsequently, the adjustment approach of the photopolymer constituent of this invention is described below. To the high molecular compound which is acid reactivity, the resin or itself containing the low-molecular matter with an acid reactivity unit adds 0.5 - 20% of the weight of a photo-oxide generating agent, and 0.1 - 20% of the weight of an acid growth agent to it. Since many of above-mentioned photo-oxide generating agents generate a radical kind with an acid, it can also mix with a radical polymerization nature monomer or a prepolymer with the acid active substance. Furthermore, a pigment, a color, etc. may be added suitably.
[0042] In order to distribute to homogeneity, it is desirable to dissolve each liquefied. It exposes, after making these constituents into the shape of film, and the acid as a latent image is

generated. Subsequently, while performing heating (postbake) processing and urging a chain of decomposition of an acid growth agent, an acid catalyzed reaction causes a structural change of the acid active substance. although the conditions of heat-treatment are changed according to the class of residue [activity / acid / exposure energy and / to be used], the class of macromolecule, etc. -- whenever [stoving temperature] -- the range of 60 to 150 degrees -- it is the range of 80 to 130 degrees more preferably. Heating time is 5 minutes from 30 seconds more preferably from 10 seconds for 10 minutes. If heating time is short more than this, an acid catalyzed reaction will not fully be triggered, in the time amount exceeding this range, an acid growth agent may trigger side reaction, and productivity is missing. The resin or itself containing the acid active substance uses change of the physical properties before and behind the exposure accompanying a structural change of the resin which is acid reactivity, and heat-treatment, for example, solubility, a degree of hardness, thickness, viscosity, gassing, etc. Furthermore, it can divide into the resin layer which contains a photo-oxide generating agent in this invention, and the resin layer containing an acid growth agent, and can consider as two-layer structure. Next, this invention is explained still more concretely with an example.
[0043]
[Example] The synthetic example of the typical acid growth agent which can be first used by this invention is shown as an example of reference.
It was made to react to the 2-methyl-3-keto butanoic acid tert butyl ester which example of reference 1 acetoacetic-acid tert-butyl ester was made to react with a methyl iodide, and obtained it under existence of the sodium hydride in THF with formalin in ethanol under existence of a potassium hydroxide. The 2-hydroxymethyl-2-methyl-3-keto butanoic acid tert butyl ester generated at 40% of yield was made to react with p-tosyl chloride under existence of triethylamine in dichloromethane, and 2-methyl-2-(p-toluenesulfonyloxy)-3-keto butanoic acid tert butyl ester was obtained as oily matter. The product was refined by silica gel column chromatography -.
m. p.52-53-degree-C1 H-NMR (CDCl3)
delta (ppm):1.38 (s, 3H, and -COC(CH3) CO-), 1.40 (s, 9H, -C3 (CH3)) 2.15 (s, and 3H and CH3CO-), 2.47 (s, 3H, Ar-CH3), 4.28 (ABq, J= 10Hz, 2H, and -CH2-OSO2-), 7.38 (d, J= 7.7Hz, 2H, Ar-H), 7.77 (d, J= 7.7Hz, 2H, Ar-H)
IR(cm~1): 1738 (>C=O of ester) 3000, 1719 (>C=O)
Elemental-analysis C17H24O6Scalc. C:57.29% H:6.79% S:9.00%found C:57.18% H:6.90% S:8.84%
[0044] Like example of reference 2 example 1, methansulfonic acid chloride was used instead of p-tosyl chloride, and 2-methyl-2-methane sulfonyloxy-3-keto butanoic acid tert butyl ester was obtained as oily matter.
1H-NMR(CDCl3)
delta (ppm):1.50 (s, 12H, -C3 (CH3)), -COC(CH3) CO-, 2.22 (s, and 3H and CH3CO-), 3.05 (s, 3H, -OSO2CH3), 4.50 (s, and 2H and -CH2-OSO2-)
13C-NMR(CDCl3)
delta (ppm):17.2 (CH3), and 27.2 (CH3), 27.5 (CH3), 36.9 (CH3), 59.9 (>C -- <), 71.1 (>C -- <), 83.1 (CH2), 168.3 (C=O) and 202.7 (C=O)
IR(cm~1): 1738 (>C=O of ester) 2981, 1714 (>C=O)
Elemental-analysis C11H20O4Scalc. C:47.13% H:7.19% S:11.44%found C:47.33% H:7.45% It was made to react with 2-phenyl-2-propanol, having used sodium acetate as the catalyst, and example of S:10.3% reference 3 diketene was made into acetoacetic-acid 2-phenyl-2-propyl ester. The hydroxymethyl derivative obtained by performing methylation and methylol-ization like an example 1 in this was made to react with p-tosyl chloride, and 2-methyl-2-(p-toluenesulfonyloxy)-3-keto butanoic acid 2-phenyl-2-propyl ester was obtained as oily matter.
1H-NMR(CDCl3)
delta (ppm):1.39 (s, 3H, and -COC(CH3) CO-), 1.75 (-O-C [3H and] (CH3) 2-) 1.79 (s, and 3H and -O-C (CH3) 2-), [s, and] 2.12 (CH [3H and]3CO-) 2.44 (s, 3H, Ar-CH3), [s, and] 4.30 (ABq, J= 14Hz, 2H, and -CH2-OSO2-), 7.30 (s, 5H, Ar-H), 7.35 (d, J= 8.7Hz, 2H, Ar-H), 7.74 (d, J= 8.7Hz, 2H, Ar-H)
IR(cm~1): 1738 (>C=O of ester) 2983, 1716 (>C=O)

Elemental-analysis C22H26O6Scalc. C:63.14% H:6.26% S:7.66%found C:62.98% H:6.48% S:6.76%
[0045] The methylol-ized acetoacetic-acid 2-phenyl-2-propyl ester which was obtained in the example of reference 4 example 3 was made to react with methane sulfonyl chloride, and 2-methyl-2-methane sulfonyloxy-3-keto butanoic acid 2-phenyl-2-propyl ester was obtained as oily matter.
1H-NMR(CDCl3)
delta (ppm):1.49 (s, 3H, and -COC(CH3) CO-), 1.75 (-O-C [3H and] (CH3) 2-) 1.80 (s, and 3H and -O-C (CH3) 2-), [s, and] 2.20 (s, and 3H and CH3CO-), 2.90 (s, 3H, -SO2CH3), 4.48 (dd, J= 13Hz, 2H, and -CH2-O-), 7.30 (s, 5H, Ar-H)
IR: 1738 (>C=O of ester) 2985, 1714 (>C=O)
The example of reference 51-methyl hexene was oxidized under existence of osmium oxide, and the cis--1-methyl 1 and 2-dihydroxy hexane were obtained. This was made to react under existence of p-tosyl chloride and triethylamine, and the cis--1-methyl-1-hydroxy-2-(p-toluenesulfonyloxy) hexane was obtained at 82% of yield.
Colorless prism ** m.p.65-66 degree-CIR (KBr) 3460, 2935, 1598, and 1348, 1176cm~1, 1 H-NMR delta= 1.1 (s, and 3H and -CCH3 (OH)-) (60MHz, CDCl3), 1.9 (s, 1H, OH) 1.1-2.0 (m, 8H, -(CH2) 4-), 2.5 (s, 3H, Ar-CH3), 4.3 (ABq, 1H, and -CH(OTs)-, J = 5 or 9Hz), 7.4 (d, 2H, Ar-H, J= 8Hz), 7.8 (d, 2H, Ar-H, J= 8Hz)
[0046] The example of reference 62-methyl-3-hydroxy propene was oxidized by the tert-butyl hydroperoxide under existence of triphenyl phosphine, and the 1 and 2-epoxy-2-methyl-3-hydroxy propane was obtained. This was made to react with p-tosyl chloride under existence of triethylamine, and the 1 and 2-epoxy-2-methyl-3-(p-toluenesulfonyloxy) propane was obtained. The colorless oily matter (NaCl) 1600 and IR 1364, 1192 or 1178cm~11 H-NMR (60MHz, CDCl3) delta= 1.3 (s, 3H, CH3), 2.5 (s, 3H, Ar-CH3), 2.9 (s, and 2H and -CH2O-), 7.4 (d, 2H, Ar-H, J= 8Hz), 7.8 (d, 2H, Ar-H, J= 8Hz)
After ketal-izing example of reference 7 benzoylacetic-acid ethyl ester by ethylene KURIKO-RU, it returned with lithium hydride aluminum and considered as the 3-phenyl -3 and 3-ethylene dioxy propanol -1. p-tosyl chloride was made to react to this under existence of triethylamine, and the crystalline 1-(p-toluenesulfonyloxy)-3-phenyl -3 and 3-ethylene dioxy propane were obtained with about 70% of yield.
Colorless oily matter m.p.48-50 degree-CIR (KBr) 2892, 1597, and 1354, 1178cm~1, 1 H-NMR delta= 2.27 (t, 2H, -CH2CH2OTs, J= 8Hz) (90MHz, CDCl3), 2.44 (s, 3H, Ar-CH3) and 3.6- 4.1 (m, 4H, and -OCH2CH2O-), 4.15 (t, 2H, -CH2CH2OTs, J= 8Hz), and 7.2- 7.5 (m, 7H, Ar-H) and 7.76 (d, 2H, Ar-H, J= 8Hz)
[0047] The 4-% of the weight cyclohexane solution of example 1 Pori (p-(tert-buthoxycarbonyloxy) styrene) was prepared, and the diphenyl (p-phenylthiophenyl) sulfonium hexafluoroantimonate which is 5% of the weight (it is two-mol % to a monomeric unit) of a photo-oxide generating agent was dissolved to this polymer. Addition of the 2-methyl-2-(p-toluenesulfonyloxy)-3-keto butanoic acid tert butyl ester which is the acid growth agent obtained in the example 1 of reference in this solution was carried out to this polymer 10% of the weight (it is six-mol % to a monomeric unit). It considered as the thin film which carries out spin spreading of this solution on a silicon wafer, and has 0.5-micrometer thickness, and prebake processing was performed for this for 1 minute at 100 degrees C. For the comparison, the poly membrane which does not contain an acid growth agent was prepared similarly. These poly membranes were drawn for 7 minutes, and after changing time amount and carrying out UV irradiation of each, postbake processing was performed at 100 degrees C. Since the acid decomposed and thickness reduced this macromolecule, thickness change was measured and the sensitization rate was evaluated. To the acidolysis of a macromolecule being completed by exposure for 17 seconds, when an acid magnification agent is added, in the acid growth agent additive-free case, in order for the reduction in thickness to be about 25% and to dissolve completely in the exposure for 17 seconds, the exposure for 50 seconds was required by the postbake for 2 minutes. Moreover, when an acid growth agent was added, reduction of the thickness in postbake has taken place rapidly, and the magnification effectiveness was accepted clearly. Image formation was checked by carrying out postbake processing behind the bottom of

exposure through a mask.
[0048] Instead of the diphenyl (p-phenylthiophenyl) sulfonium hexafluoroantimonate used as a photo-oxide generating agent in example 2 example 1, 6% of the weight of 2 and a 3-diphenyl-3-keto-2-hydroxy-1-(p-toluenesulfonyloxy) propane were added as a photo-oxide generating agent, and the addition effectiveness of the 2-methyl-2-(p-toluenesulfonyloxy)-3-keto butanoic acid tert butyl ester obtained in the example 1 of reference was investigated. After carrying out spin spreading of the thin film on a silicon wafer like an example 1, postbake was performed at 100 degrees C for 3 minutes after carrying out ultraviolet-rays exposure. In the acid growth agent additive-free case, although reduction of the thickness containing an acid growth agent was rapidly completed by the exposure for 60 seconds, by the same exposure time, thickness decreased only about 15%, but in order to complete thickness reduction, it required the exposure time for 180 seconds.
3.4% of the weight of triphenylsulfonium triflate and the 2-methyl-2-(p-toluenesulfonyloxy)-3-keto butanoic acid tert butyl ester which is 1% of the weight of an acid growth agent were added to the cyclohexane solution of a polymer used in the example 3 example 1 to the polymer, and the thin film was prepared. After exposing ultraviolet rays, when postbake was performed at 100 degrees C for 3 minutes, the reduction in thickness was completed by the exposure for 55 seconds. In order in an additive-free case to remain in reduction of about 15% of thickness and to complete an acid growth agent by the same exposure time, the exposure time for 150 seconds was required.
[0049] 10% of the weight of diphenyl (p-phenylthiophenyl) sulfonium hexafluoroantimonate and the cis--1-methyl-1-hydroxy-2-(p-toluenesulfonyloxy) hexane obtained in the example 5 of reference were added to the cyclohexane solution of a polymer used in the example 4 example 1 5% of the weight to the polymer, and on the silicon wafer, spin spreading was carried out and it considered as the 0.5-micrometer thin film. After performing postbake for 2 minutes at 100 degrees C after exposing ultraviolet rays, negatives were developed by ethanol, and the residual membrane was measured. Although all film dissolved by the exposure time for 10 seconds when an acid growth agent was added, the exposure time for 70 seconds or more was required of additive-free.
The 1 and 2-epoxy-2-methyl-3-hydroxy propane compounded in the example 6 of reference instead of the cis--1-methyl-1-hydroxy-2-(p-toluenesulfonyloxy) hexane used in example 5 example 4 was added. When UV irradiation, postbake processing, and ethanol development were performed similarly, the exposure time required in order to dissolve all film by adding an acid growth agent was able to be shortened to the quadrant.
[0050] 10% of the weight of diphenyl (p-phenylthiophenyl) sulfonium hexafluoroantimonate and the cis--1-methyl-1-hydroxy-2-(p-toluenesulfonyloxy) hexane obtained in the example 5 of reference were added to 2:1 copolymers (Mw=4.01x104, Mw/Mn=1.74) of example 6 methyl methacrylate and methacrylic-acid 2-phenyl-2-propyl ester 5% of the weight, and on the silicon wafer, spin spreading was carried out and it considered as the 0.23-micrometer thin film. After irradiating ultraviolet rays at this, postbake processing was performed for 2 minutes at 100 degrees C, negatives were developed by ethanol, and the remaining rate of membrane was measured. By adding an acid growth agent, the exposure time required for becoming residual membrane zero was able to be shortened to the quadrant.
Same exposure, postbake, and ethanol development were performed using the 1-(p-toluenesulfonyloxy)-3-phenyl -3 and 3-ethylene dioxy propane which were compounded in the example 7 of reference instead of the cis--1-methyl-1-hydroxy-2-(p-toluenesulfonyloxy) hexane used in example 7 example 6. By adding this acid growth agent, the exposure time for solubilizing all film was able to be shortened to about 1/3.
[0051] In the cyclohexanone solution of a polymer used in the example 8 example 1, the diphenyl (p-phenylthiophenyl) sulfonium hexafluoroantimonate which is a photo-oxide generating agent, and the 1-(p-toluenesulfonyloxy)-3-phenyl -3 and 3-ethylene dioxy propane were added 10% of the weight to the polymer, respectively, and on the silicon wafer of three sheets, spin spreading was carried out, respectively and it considered as the 0.25-micrometer thin film. After irradiating ultraviolet rays through the fenestera rotunda with a diameter of 3mm at these thin films, it

heat-treated at 105 degrees C, 115 degrees C, and 125 degrees C. After the discoloration accompanying reduction in thickness appeared immediately as a round shape which is 3mm, the round shape increased with time amount. Postbake time amount until a diameter is set to 12mm was 30 seconds by 125 degrees C for 45 seconds at 115 degrees C in 105 degrees C for 7 minutes. This is because the acid generated with light is spread with heating within a poly membrane and acid generating by decomposition of an acid growth agent is caused one after another in connection with it. When an acid growth agent was not added, such reduction did not take place.
[0052] % of the 15-mol 1-(p-toluenesulfonyloxy)-3-phenyl -3 as two-mol % 2, and the 3-diphenyl-3-keto-2-hydroxy-1-(p-TORUHEN sulfonyloxy) propane and the acid growth agent as a photo-oxide generating agent and 3-ethylene dioxy propane were added to the solution of 2-methoxy ethyl acetate of an example 9p-trimethylsilyloxy styrene homopolymer (5.35x104, Mw/Mn=1.69). After carrying out spin spreading of this solution by 1000rpm on the silicon wafer and carrying out prebake for 30 seconds at 100 degrees C, time amount was changed, ultraviolet rays were irradiated and postbake was given for 30 seconds at 100 degrees C. When it was immersed for 10 seconds into ethanol and negatives were developed, the exposure time which a poly membrane solubilizes completely was shortened to about 1/3 compared with acid growth agent additive-free.
After adding 3% of the weight of diphenyl (p-phenylthiophenyl) sulfonium hexafluoroantimonate, and 3% of the weight of 2-methyl-2-(p-toluenesulfonyloxy)-3-keto butanoic acid tert butyl ester to the cyclohexane solution of 1:1 copolymers (Mw=5.15x104, Mw/Mn=2.04) of example 10 methyl methacrylate and glycidyl methacrylate to this polymer, spin spreading was carried out on the anodized aluminum plate. To this, time amount was changed, ultraviolet rays were exposed, and after carrying out postbake at 100 degrees C for 3 minutes, the plate was washed with toluene. When compared with the case where an acid growth agent is not added, the exposure time which insolubilization of a copolymer takes was shortened to 1/5.
[0053] Addition of the 2-methyl-2-(p-toluenesulfonyloxy)-3-keto butanoic acid tert butyl ester which is the acid growth agent obtained in the example 1 of reference in the cyclohexane solution of a polymer used in the example 11 example 1 was carried out to this polymer 10% of the weight (it is six-mol % to a monomeric unit). It considered as the thin film which carries out spin spreading of this solution on a silicon wafer, and has 0.27-micrometer thickness, and prebake processing was performed for this for 1 minute at 100 degrees C. For the comparison, the poly membrane which does not contain an acid growth agent was prepared similarly. 3.5% of the weight of triphenylsulfonium TORIFURA-TO was dissolved in the 0.07-% of the weight isopropyl alcohol solution of novolak resin to resin, and spin spreading was carried out on the poly membrane which prepared this previously. Prebaking for 1 minute at 100 degrees C, the film which consists of two-layer [of the film containing a photo-oxide generating agent and the film containing an acid growth agent] became the thickness of 0.62 micrometers as a whole. After exposing ultraviolet rays on this two-layer film, postbake processing was performed at 100 degrees C, and negatives were developed in 40-degree C ethanol for 1 minute. When asked for the relation between the exposure time and a remaining rate of membrane, having high-sensitivity-ized the two-layer film which added the acid growth agent 20 times compared with the additive-free two-layer film was admitted.
[0054] In example 12 example 11, when the completely same exposure as an example 10 was performed about the film of the two-layer structure which added triphenylsulfonium hexafluoroantimonate instead of triphenylsulfonium TORIFURA-TO as a photo-oxide generating agent, 18 times as many high sensitivity-ization as this was accepted by addition of an acid growth agent.
The sensibility of the film of the two-layer structure which added the triphenylsulfonium hexafluoroantimonate prepared in the example 13 example 11, and the film which added triphenylsulfonium hexafluoroantimonate to the polymer of the example 1 which is a well-known chemistry magnification mold photoresist was measured. Consequently, the film of the two-layer structured type which separates and contains an acid growth agent showed 25 times as many high sensitivity as this to the chemistry magnification resist.

[0055]
[Effect of the Invention]
(1) Since a sensitization rate improves sharply, it can use for a high sensitivity image formation ingredient.
(2) Since the bridge formation effectiveness of photo-curing resin improves sharply by combining an optical exposure and heat-treatment, it can use to an ultraviolet curing mold coating, ink, a surface coating agent, etc. effectively. In the paint film which consists of a photo-curing agent which carried out pigment-content powder, although it does not happen at all in that hardening is inadequate or the interior since light absorption happens only by the surface layer, according to this invention, hardening can be made perfect by heat-treatment after an optical exposure.
(3) Since the yield of an acid increases sharply by the acid growth agent, it can reduce the amount of the photo-oxide generating agent used. Consequently, since light can fully permeate to the interior of a sensitization layer, it becomes possible to increase the thickness of a sensitization layer of it sharply.

[Translation done.]

TECHNICAL FIELD

[Industrial Application] This invention relates to the acid reactive polymer constituent and acid reactivity resin layer containing this photoreaction constituent further about the photoreaction constituent which raised the sensitization rate by combining the matter (it being hereafter called an acid growth agent) which newly generates an acid with the generated acid with the matter (it being hereafter called a photo-oxide generating agent) which generates an acid in an operation of light.

[Translation done.]

PRIOR ART

[Description of the Prior Art] Light energy is absorbed conventionally and it is used in the direction chemical between intramolecular or a molecule or of versatility [ingredient / which has the photosensitive function which produces a physical change]. For example, in many fields, it is used and using as an image formation ingredient which detects optically the chemical structural change produced by the photoreaction, or using as a surface coating processing ingredient which performs surface treatment by the photo-curing of a monomer or a prepolymer etc. is put in practical use. However, the sensitization rate in the ingredient which has these photosensitive functions, a sensitization wavelength field, and definition are various, and the ingredient which has a suitable property according to the purpose is chosen.
[0003] Although silver salt sensitive material was used more widely in ancient times as an ingredient which has a photosensitive function, the photopolymer which uses polymeric materials as a principal component reaches far and wide as extensive and the high sensitivity image formation ingredient in which high definition is shown, and it came (refer to the volume Yamaoka Tsugio and for Gentaro Matsunaga, "photopolymer technology", and Nikkan Kogyo Shimbun (1988)) to be used in recent years. [as / in a photoengraving-process technique etc.] The macromolecule system photosensitivity ingredient is not only excellent in definition, but can set up a wide range sensitization wavelength field by selection of the photoreaction. Moreover, it has many advantages of being able to manufacture comparatively cheaply. However, a sensitization rate is very low in comparing with a silver salt photosensitivity ingredient, and also although it is called the high sensitivity macromolecule system photosensitivity ingredient, the present condition is not amounting to 1/1000 of the sensitization rate which a silver salt ingredient's shows.
[0004] In order to raise the sensitization rate of a macromolecule system photosensitivity ingredient, various attempts have so far been made. It is the photopolymerization system to which having been most widely set as the object of development carries out the polymerization of many vinyl monomers continuously by making into an initiator the radical kind generated in an operation of light. However, since the oxygen in air and the radical kind which reacts easily are growth kinds, it ends, without completing sufficient chain reaction. Moreover, with advance of a radical polymerization reaction, diffusion of a monomer is quickly controlled for the network structure within the macromolecule matrix formed rapidly, and a polymerization cannot be completed. For such a cause, essential threshold value exists in the sensitization rate of a photopolymerization system.
[0005] Creation of various macromolecule system photosensitivity ingredients was attained by generating an acid in an operation of light and on the other hand, combining not only the cationic polymerization that makes this acid a catalyst but various acid catalyzed reactions. Although high sensitivity is expected since there is no halt effectiveness of the reaction by oxygen unlike a radical polymerization, the sensitization rate of the present condition is rather lower in cationic polymerization, than a radical polymerization system in fact for the moisture in air, or network structure formation. Moreover, let it be a principle to heat-treat, after generating an acid with light, and to carry out induction of the acid catalyzed reaction with the macromolecule system photosensitivity ingredient incorporating an acid catalyzed reaction. For this reason, this kind

that makes a photoresist a main use gestalt of giant-molecule system photosensitivity ingredient is called the chemistry magnification mold photoresist. However, the present condition is that a sensitization rate is less than a radical polymerization system, and improvement in a fast sensitization rate has still been called for.

[0006] Furthermore, by using an optical radical polymerization and optical cationic polymerization, or combining the both, the resin constituent which hardens a film-like resin coat to a high degree of hardness by optical exposure is also large liquefied, and practical use is presented. Although the optical cationic polymerization system which does not receive the inhibition effectiveness by the oxygen in air is widely set as the object of development research and development of the monomer and prepolymer suitable for the photo-oxide generating agent suitable for hardening or hardening is performed actively in recent years, improvement in a cure rate is called for for speeding up of a hardening process. Furthermore, since hardening of the resin constituent and the thick coat which the pigment which absorbs light distributed takes place only by the surface layer, the essential trouble that sufficient hardening is not brought about has resulted as it is not solved. Moreover, it thinks for the base component of the minute amount which floats in air to bring about a poisoning operation of a catalyst as a cause by which it will not become so high although the sensitization rate of the above-mentioned chemistry magnification mold photoresist uses the acid catalyzed reaction, or the acid catalyzed reaction in the inside of a macromolecule matrix triggers side reaction, and it is also considered that an acid catalyzed reaction stops for this reason.

[0007]

[Translation done.]

EFFECT OF THE INVENTION

[Effect of the Invention]
(1) Since a sensitization rate improves sharply, it can use for a high sensitivity image formation ingredient.
(2) Since the bridge formation effectiveness of photo-curing resin improves sharply by combining an optical exposure and heat-treatment, it can use to an ultraviolet curing mold coating, ink, a surface coating agent, etc. effectively. In the paint film which consists of a photo-curing agent which carried out pigment-content powder, although it does not happen at all in that hardening is inadequate or the interior since light absorption happens only by the surface layer, according to this invention, hardening can be made perfect by heat-treatment after an optical exposure.
(3) Since the yield of an acid increases sharply by the acid growth agent, it can reduce the amount of the photo-oxide generating agent used. Consequently, since light can fully permeate to the interior of a sensitization layer, it becomes possible to increase the thickness of a sensitization layer of it sharply.

[Translation done.]

TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] The result to which this invention person examined various the approaches of solving such a situation radically, It is what completed a header and this invention for the photoreaction constituent which raised the sensitization rate remarkably by combining the matter which newly generates an acid with the generated acid with the matter which generates an acid in an operation of light. The purpose of this invention offers the photoreaction constituent which was made to amplify photochemical reaction and raised the sensitization rate remarkably.

[Translation done.]

MEANS

[Means for Solving the Problem] The photo-oxide generating agent in which the summary of invention of the 1st of this application generates an acid according to an operation of light, It is the photoreaction nature constituent which consists of an acid growth agent which newly generates an acid with the acid generated from this photo-oxide generating agent. The photo-oxide generating agent which generates an acid according to an operation of light in the high polymer which mixed the matter from which the summary of the 2nd invention produces molecular structure change according to an operation of an acid, or the high polymer which combined the residue which produces molecular structure change according to an operation of an acid, It is the acid reactive polymer constituent characterized by making the acid growth agent which newly generates an acid according to an operation of this acid exist. The high polymer which mixed the matter from which the summary of the 3rd invention produces molecular structure change according to an operation of an acid, Or the acid growth agent which newly generates an acid with the acid generated from said photo-oxide generating agent in the resin layer which consists of a high polymer which combined the residue which produces molecular structure change according to an operation of an acid, and a photo-oxide generating agent, The aforementioned resin layer which consists of a high polymer which mixed the matter which produces molecular structure change according to an operation of the newly generated acid, or a high polymer which combined the residue which produces molecular structure change according to an operation of an acid is an acid reactivity resin layer which has the two-layer structure which carried out the laminating of the different resin layer. Namely, by combining with a photo-oxide generating agent the acid growth agent which newly generates an acid according to an operation of an acid in this invention Since one acid is generated, and this acid disassembles an acid growth agent molecule and newly generates one or more acids from a photo-oxide generating agent according to an operation of light One or more acid-content children will increase at one reaction, it will become a total of two or more acid-content children, this reaction will arise continuously, and generating of an acid will increase in multiplying like rats. That is, by addition, an acid can also prevent a halt of the acid catalyzed reaction by increase, consequently the alkali rapidly, and disappearance of the acid by side reaction can also prevent an acid growth agent with such a property, and an acid catalyzed reaction can be accelerated sharply. It is as follows when the principle of an above-mentioned reaction principle is illustrated.

$AG \longrightarrow H^{+}$ ……………… 光酸発生

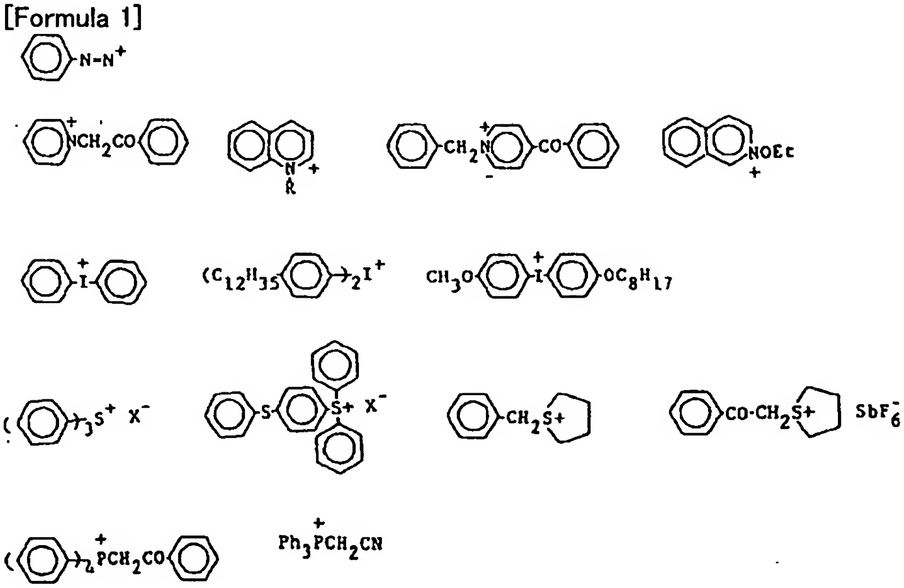
$\downarrow$

$m \times X \longrightarrow m \times H^{+}$ ………… 酸増殖反応

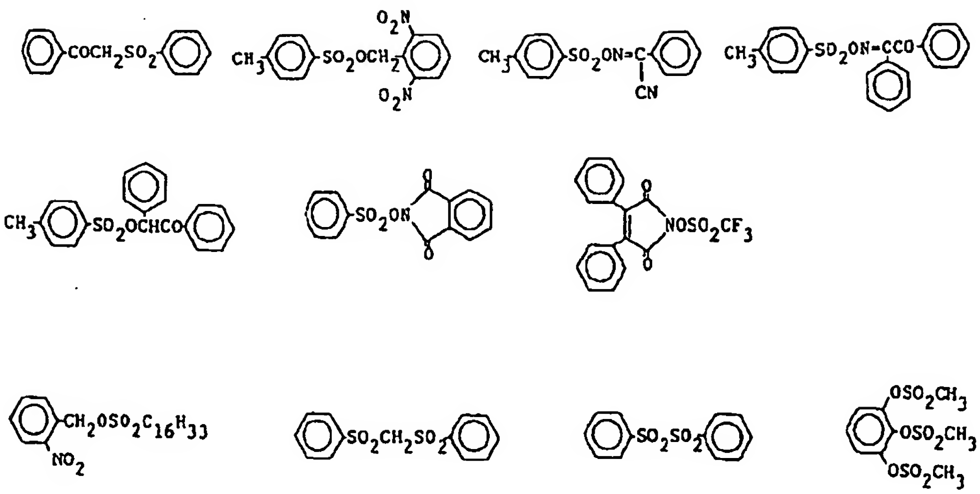
$\downarrow$

$n \times M \longrightarrow n \times N$ ……… 酸触媒反応

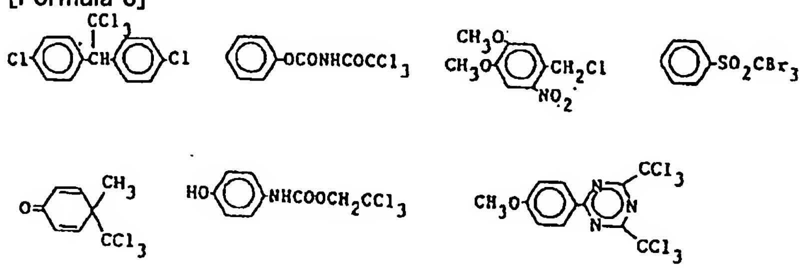
AG Photo-oxide generating agent; X Acid growth agent;M Acidolysis product; N The acidolysis products m and n are molecularity. The organic compound which increases such an acid was used, and the growth reaction which generates an acid in multiplying like rats was not known at all as an organic chemistry reaction until now, although it was similar to a nuclear fission reaction

or explosive reaction. Although it is thermally stable as much as possible, an acid decomposes and an acid growth agent generates strong acid itself, it is the compound permuted by the residue of a comparatively strong acid, and triggers an elimination reaction comparatively easily and generates an acid. Therefore, although it is stable under un-existing [of an acid] if this elimination reaction can be sharply activated by the acid catalyzed reaction, under existence of an acid, it becomes possible to make thermal reaction generate an acid easily. By combining an acid growth agent with such a property with a photo-oxide generating agent, the photosensitive ingredient whose sensitization rate improved by leaps and bounds became possible.
[0009] This invention is explained to a detail. As a photo-oxide generating agent which generates an acid according to an operation of light in this invention, the compound used for a chemistry magnification mold photoresist or optical cationic polymerization is used (the volume on organic electronics ingredient study group, "imaging business refer to organic material", the **** exudation version (1993), and 187 - 192 pages). The example of the suitable compound for this invention is given to below. Moreover, in order to expand the sensitization wavelength field of these photo-oxide generating agents, a photosensitizer can also be made to live together suitably. With the acid active substance, the acid generated by the photolysis of these matter acts on an acid growth agent, and promotes generating of an acid. The following photo-oxide generating agents can be used. PF6- of aromatic series onium compounds, such as diazonium, ammonium, iodonium, sulfonium, and phosphonium, AsF6-, SbF6-, and a CF3SO3-salt can be mentioned [1st]. The concrete example of an onium compound is shown below.
[0010]
[Formula 1]


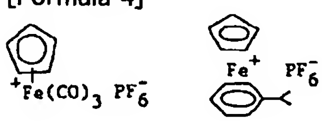
[0011] The sulfonation object which generates [2nd] a sulfonic acid can be mentioned. A concrete compound is illustrated below.
[0012]
[Formula 2]



[0013] The halogenide which carries out optical generating of the hydrogen halide can also be used [3rd]. A concrete compound is illustrated below.
[0014]
[Formula 3]

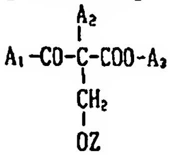


[0015] An iron allene complex can be mentioned to the 4th.
[0016]
[Formula 4]



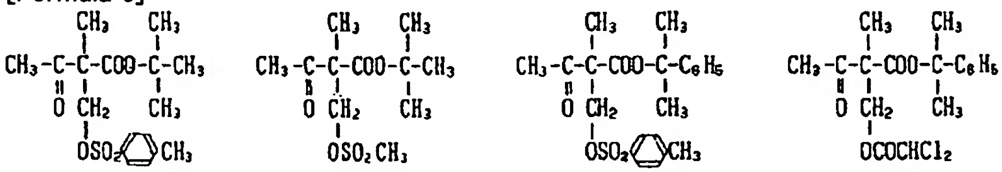
[0017] The acid growth agent used by this invention is the compound permuted by the residue of a comparatively strong acid, and is a compound which triggers an elimination reaction comparatively easily and generates an acid. Therefore, this elimination reaction can be sharply activated by the acid catalyzed reaction, and although it is stable under un-existing [of an acid], under existence of an acid, it becomes possible to make thermal reaction generate an acid easily. By combining an acid growth agent with such a property with a photo-oxide generating agent, the photoreaction nature constituent whose sensitization rate improved by leaps and bounds became possible. An acid catalyzed reaction decomposes and an acid (it is ZOH at the following general formulas) is generated again. One or more acids are increasing in number at one reaction, and a reaction progresses accelarative with advance of a reaction. In order for the generated acid itself to carry out induction of the autolysis, reinforcement of the acid generated here is set to an acid dissociation constant and electric dissociation exponent, and is three or less, and it is desirable that it is two especially or less. An autolysis cannot be caused if it is an acid weaker than this. As such an acid, dichloroacetic acid, a trichloroacetic acid, methansulfonic acid, ethane sulfonic acid, benzenesulfonic acid, p-toluenesulfonic acid, a naphthalene sulfonic acid, triphenyl phosphonic acid, etc. can be raised. Specifically, the following compounds can be illustrated. The organic-acid ester compound expressed [1st] with a general formula (1) can be mentioned.

[0018]
[Formula 5]

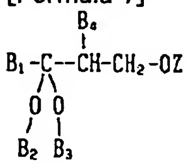


(1)

[0019] (A1 shows the alkyl group or aryl group from C1 to C6 among a formula, A2 shows the alkyl group from C1 to C6, and A3 is screw (p-alkoxy phenyl) methyl) A radical, a 2-alkyl-2-propyl group, a 2-aryl-2-propyl group, a cyclohexyl radical, or a tetrahydropyranyl group is shown, and Z shows the residue of the acid shown by ZOH whose acid dissociation constant (electric dissociation exponent) is three or less.
If an acid acts on this compound, an ester group decomposes and it becomes a carboxylic acid, and after this raises a decarboxylic acid further, an acid (ZOH) will **** easily. Specifically, an example is shown below.
[0020]
[Formula 6]

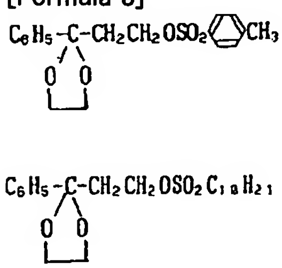


[0021] Organic-acid ester with the acetal or ketal radical expressed [2nd] with a general formula (2) can be mentioned.
[0022]
[Formula 7]

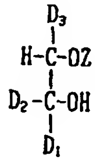


(2)

[0023] (Z has the same semantics as the above among a formula, B1 is a hydrogen atom, an alkyl group, or an aryl group, B-2 and B3 form ethylene or a propylene radical in methyl, an ethyl group, or both, and B4 shows a hydrogen atom or a methyl group)
An acetal or ketal decomposes in an operation of an acid, this compound serves as beta-aldehyde or a ketone, and ZOH is easily desorbed from it after this. A concrete example is shown below.
[0024]
[Formula 8]

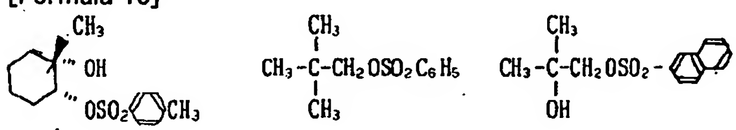


[0025] The organic-acid ester expressed [3rd] with a general formula (3) can be mentioned.
[0026]
[Formula 9]

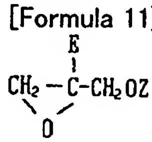


(3)

[0027] (Z has the same semantics as the above among a formula, D1 and D2 show a hydrogen atom, the alkyl groups from C1 to C6, or an aryl group, and D2 and D3 show the alkylene or permutation alkylene residue which forms alicycle-like structure on the alkyl group or both sides from C1 to C6)
After a hydroxyl group ****s, and this compound forms carbocation and carries out hydrogen migration according to an acid catalyst, it is presumed to be what ZOH generates. A concrete example is shown below.
[0028]
[Formula 10]

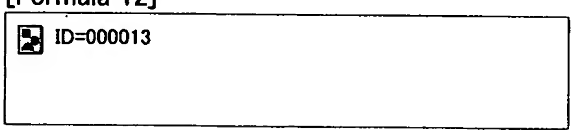


[0029] The organic-acid ester which has the epoxy ring expressed [4th] with a general formula (4) can be mentioned.
[0030]
[Formula 11]

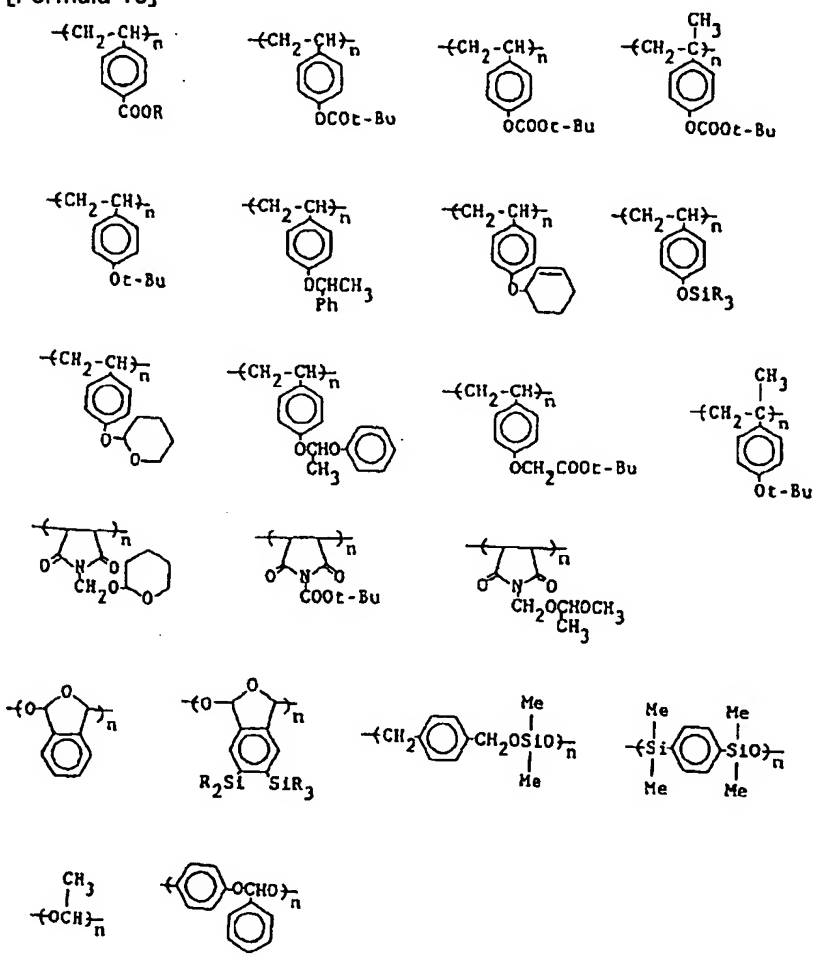


(4)

[0031] (Z has the same semantics as the above among a formula, and E shows the alkyl groups or phenyl groups from C1 to C6)
If an acid acts on this compound, a cation will be formed in beta-carbon with generation of the ring breakage of an epoxy ring, and what an organic acid generates as a result of hydrogen migration will be presumed. A concrete example is shown below.
[0032]
[Formula 12]

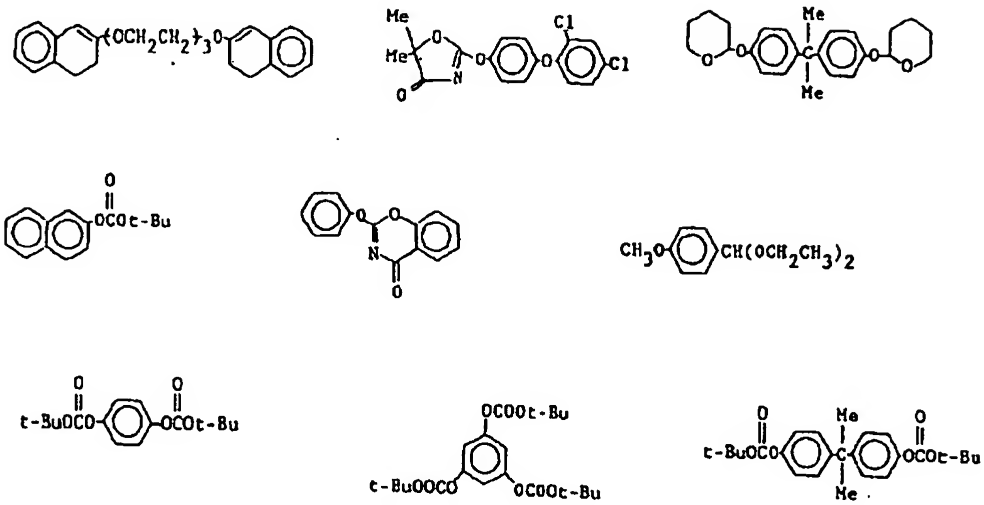


[0033] These compounds exist in stability at a room temperature, unless an acid acts. Although the acid strength more than fixed is needed in order to cause acid-catalyst disassembly of these compounds, it is desirable that it is about two or less in an acid dissociation constant pka. If it is the acid dissociation constant beyond this, i.e., a weaker acid than this, the reaction of an acid growth agent cannot be triggered.
[0034] Next, the high polymer which mixed the matter (acid reactivity molecule) which produces molecular structure change according to an operation of the acid in which the above-mentioned photoreaction constituent is made to exist, or the high polymer which combined the residue which produces molecular structure change according to an operation of an acid is explained. In addition, the matter or residue which produces molecular structure change is only called an acid reactivity molecule or acid reactivity residue. The example.of a polymeric material which mixes, or joins together and becomes about the acid reactivity molecule used suitable for this invention is shown (the volume on organic electronics ingredient study group, "imaging business refer to organic material", the **** exudation version (1993), and 199 - 201 pages). many use the reaction of the deprotection radical in synthetic organic chemistry — **** (T. refer to

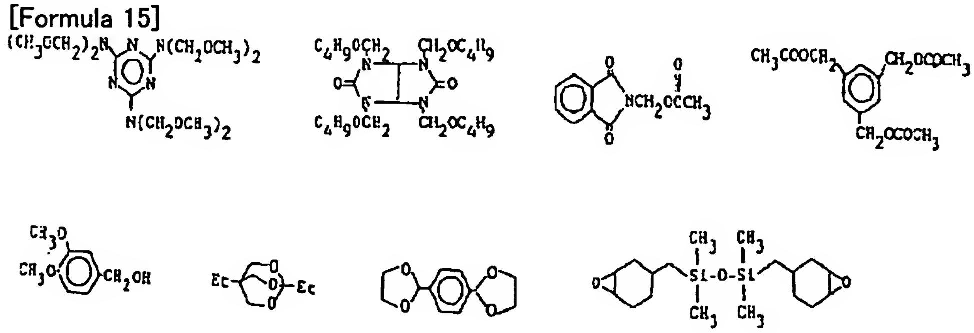
W.Greene, Protective Groups in Organic Synthesis, and John Wiley & Sons (1981)) -- a concrete example is shown below. The high polymer which has acid reactivity residue in a side chain or a principal chain can be mentioned to the 1st. As acid reactivity residue, the phenol nature or N-methylol nature hydroxyl group protected by the 2nd class, the 3rd class ester, the tetrahydropyranyl ester, the 3rd class ester of carbonic acid, trialkylsilyl group, and tetrahydropyranyl group of a carboxylic acid is used suitably. Since a deprotection reaction occurs and a polar high carboxylic acid and a polar high phenol generate these according to an operation of an acid, the exposure section is solubilized in a polar solvent or an alkali water solution. High sensitivity sensitive material is one of things using such a property. As an example of a concrete compound, it is [0035].
[Formula 13]


[0036] The high molecular compound containing an acid reactivity low molecular weight compound is in the 2nd. Here, an acid reactivity low molecular weight compound has the effectiveness of reducing the solubility of a resin compound, and is called a dissolution inhibitor. As a dissolution inhibitor, phenols, a pinacol derivative, etc. which were protected by an acetal compound, a ketal compound, the 3rd class ester of a carboxylic acid, tetrahydropyranyl ester, the 3rd class ester of carbonic acid, the trialkylsilyl group, or the tetrahydropyranyl group can be mentioned. As a resin compound containing these dissolution inhibitors, novolak resin, Pori (p-hydroxystyrene), a methacrylic-acid copolymer, N-methylol maleimide copolymer, etc. can be raised. Although a low molecular weight compound has the effectiveness which checks the solubility over the alkali water solution of these resin, by decomposing in an operation of an acid, this dissolution depressor effect is lost and a macromolecule serves as alkali solubilization. A concrete dissolution inhibitor is illustrated below.
[0037]

[Formula 14]



[0038] The condensation reaction by the acid catalyzed reaction is used [3rd] for the crosslinking reaction of a macromolecule. As residue which forms a cation and causes a condensation reaction by the acid catalyst, a benzyl alcohol derivative, a melamine derivative, N-methylol imide derivative, an acetal derivative, a vinyl ether derivative, etc. can be raised. Moreover, as generated KAOCHIN and residue which reacts, a phenol, alcohol, etc. can be mentioned and polymer ** of the giant molecule which has such residue, for example, the polymer of p-hydroxystyrene, novolak resin, and hydroxyethyl methacrylate is used suitably. The compound which causes a condensation reaction is illustrated below.
[0039]
[Formula 15]



[0040] Moreover, since the macromolecule having this condensation nature residue and phenyl residue causes bridge formation by the acid catalyst by itself, it is convenient for this invention. A macromolecule with the residue which carries out [4th] a polymerization according to an acid catalyst is used. As cationic polymerization nature residue, an epoxy group, oxetane residue, a vinyl ether radical, an isopropenyl phenyl group, annular orthochromatic ester, etc. can be raised. The constituent set to the 5th from a cationic polymerization nature monomer or a prepolymer is also used. As a cationic monomeric unit, an epoxy group, an oxetane radical, a vinyl ether radical, and annular orthochromatic ester are used. It is desirable to mix with a vinyl system polymer and to use these monomers or prepolymers as a free-standing filmy material.
[0041] Subsequently, the adjustment approach of the photopolymer constituent of this invention is described below. To the high molecular compound which is acid reactivity, the resin or itself containing the low-molecular matter with an acid reactivity unit adds 0.5 - 20% of the weight of a photo-oxide generating agent, and 0.1 - 20% of the weight of an acid growth agent to it. Since many of above-mentioned photo-oxide generating agents generate a radical kind with an acid, it can also mix with a radical polymerization nature monomer or a prepolymer with the acid active substance. Furthermore, a pigment, a color, etc. may be added suitably.
[0042] In order to distribute to homogeneity, it is desirable to dissolve each liquefied. It exposes,

after making these constituents into the shape of film, and the acid as a latent image is generated. Subsequently, while performing heating (postbake) processing and urging a chain of decomposition of an acid growth agent, an acid catalyzed reaction causes a structural change of the acid active substance. although the conditions of heat-treatment are changed according to the class of residue [activity / acid / exposure energy and / to be used], the class of macromolecule, etc. -- whenever [stoving temperature] -- the range of 60 to 150 degrees -- it is the range of 80 to 130 degrees more preferably. Heating time is 5 minutes from 30 seconds more preferably from 10 seconds for 10 minutes. If heating time is short more than this, an acid catalyzed reaction will not fully be triggered, in the time amount exceeding this range, an acid growth agent may trigger side reaction, and productivity is missing. The resin or itself containing the acid active substance uses change of the physical properties before and behind the exposure accompanying a structural change of the resin which is acid reactivity, and heat-treatment, for example, solubility, a degree of hardness, thickness, viscosity, gassing, etc. Furthermore, it can divide into the resin layer which contains a photo-oxide generating agent in this invention, and the resin layer containing an acid growth agent, and can consider as two-layer structure. Next, this invention is explained still more concretely with an example.

[Translation done.]

EXAMPLE

[Example] The synthetic example of the typical acid growth agent which can be first used by this invention is shown as an example of reference.
It was made to react to the 2-methyl-3-keto butanoic acid tert butyl ester which example of reference 1 acetoacetic-acid tert-butyl ester was made to react with a methyl iodide, and obtained it under existence of the sodium hydride in THF with formalin in ethanol under existence of a potassium hydroxide. The 2-hydroxymethyl-2-methyl-3-keto butanoic acid tert butyl ester generated at 40% of yield was made to react with p-tosyl chloride under existence of triethylamine in dichloromethane, and 2-methyl-2-(p-toluenesulfonyloxy)-3-keto butanoic acid tert butyl ester was obtained as oily matter. The product was refined by silica gel column chromatography -.
m. p.52-53-degree-C1 H-NMR (CDCl3)
delta (ppm):1.38 (s, 3H, and -COC(CH3) CO-), 1.40 (s, 9H, -C3 (CH3)) 2.15 (s, and 3H and CH3CO-), 2.47 (s, 3H, Ar-CH3), 4.28 (ABq, J= 10Hz, 2H, and -CH2-OSO2-), 7.38 (d, J= 7.7Hz, 2H, Ar-H), 7.77 (d, J= 7.7Hz, 2H, Ar-H)
IR(cm~1): 1738 (>C=O of ester) 3000, 1719 (>C=O)
Elemental-analysis C17H24O6Scalc. C:57.29% H:6.79% S:9.00%found C:57.18% H:6.90% S:8.84%
[0044] Like example of reference 2 example 1, methansulfonic acid chloride was used instead of p-tosyl chloride, and 2-methyl-2-methane sulfonyloxy-3-keto butanoic acid tert butyl ester was obtained as oily matter.
1H-NMR(CDCl3)
delta (ppm):1.50 (s, 12H, -C3 (CH3)), -COC(CH3) CO-, 2.22 (s, and 3H and CH3CO-), 3.05 (s, 3H, -OSO2CH3), 4.50 (s, and 2H and -CH2-OSO2-)
13C-NMR(CDCl3)
delta (ppm):17.2 (CH3), and 27.2 (CH3), 27.5 (CH3), 36.9 (CH3), 59.9 (>C — <), 71.1 (>C — <), 83.1 (CH2), 168.3 (C=O) and 202.7 (C=O)
IR(cm~1): 1738 (>C=O of ester) 2981, 1714 (>C=O)
Elemental-analysis C11H20O4Scalc. C:47.13% H:7.19% S:11.44%found C:47.33% H:7.45% It was made to react with 2-phenyl-2-propanol, having used sodium acetate as the catalyst, and example of S:10.3% reference 3 diketene was made into acetoacetic-acid 2-phenyl-2-propyl ester. The hydroxymethyl derivative obtained by performing methylation and methylol-ization like an example 1 in this was made to react with p-tosyl chloride, and 2-methyl-2-(p-toluenesulfonyloxy)-3-keto butanoic acid 2-phenyl-2-propyl ester was obtained as oily matter.
1H-NMR(CDCl3)
delta (ppm):1.39 (s, 3H, and -COC(CH3) CO-), 1.75 (-O-C [3H and] (CH3) 2-) 1.79 (s, and 3H and -O-C (CH3) 2-), [s, and] 2.12 (CH [3H and]3CO-) 2.44 (s, 3H, Ar-CH3), [s, and] 4.30 (ABq, J= 14Hz, 2H, and -CH2-OSO2-), 7.30 (s, 5H, Ar-H), 7.35 (d, J= 8.7Hz, 2H, Ar-H), 7.74 (d, J= 8.7Hz, 2H, Ar-H)
IR(cm~1): 1738 (>C=O of ester) 2983, 1716 (>C=O)
Elemental-analysis C22H26O6Scalc. C:63.14% H:6.26% S:7.66%found C:62.98% H:6.48% S:6.76%
[0045] The methylol-ized acetoacetic-acid 2-phenyl-2-propyl ester which was obtained in the example of reference 4 example 3 was made to react with methane sulfonyl chloride, and 2-

methyl-2-methane sulfonyloxy-3-keto butanoic acid 2-phenyl-2-propyl ester was obtained as oily matter.
1H-NMR(CDCl3)
delta (ppm):1.49 (s, 3H, and -COC(CH3) CO-), 1.75 (-O-C [3H and] (CH3) 2-) 1.80 (s, and 3H and -O-C (CH3) 2-), [s, and] 2.20 (s, and 3H and CH3CO-), 2.90 (s, 3H, -SO2CH3), 4.48 (dd, J= 13Hz, 2H, and -CH2-O-), 7.30 (s, 5H, Ar-H)
IR: 1738 (>C=O of ester) 2985, 1714 (>C=O)
The example of reference 51-methyl hexene was oxidized under existence of osmium oxide, and the cis--1-methyl 1 and 2-dihydroxy hexane were obtained. This was made to react under existence of p-tosyl chloride and triethylamine, and the cis--1-methyl-1-hydroxy-2-(p-toluenesulfonyloxy) hexane was obtained at 82% of yield.
Colorless prism ** m.p.65-66 degree-CIR (KBr) 3460, 2935, 1598, and 1348, 1176cm~1, 1 H-NMR delta= 1.1 (s, and 3H and -CCH3 (OH)-) (60MHz, CDCl3), 1.9 (s, 1H, OH) 1.1-2.0 (m, 8H, -(CH2) 4-), 2.5 (s, 3H, Ar-CH3), 4.3 (ABq, 1H, and -CH(OTs)-, J = 5 or 9Hz), 7.4 (d, 2H, Ar-H, J= 8Hz), 7.8 (d, 2H, Ar-H, J= 8Hz)
[0046] The example of reference 62-methyl-3-hydroxy propene was oxidized by the tert-butyl hydroperoxide under existence of triphenyl phosphine, and the 1 and 2-epoxy-2-methyl-3-hydroxy propane was obtained. This was made to react with p-tosyl chloride under existence of triethylamine, and the 1 and 2-epoxy-2-methyl-3-(p-toluenesulfonyloxy) propane was obtained. The colorless oily matter (NaCl) 1600 and IR 1364, 1192 or 1178cm~11 H-NMR (60MHz, CDCl3) delta= 1.3 (s, 3H, CH3), 2.5 (s, 3H, Ar-CH3), 2.9 (s, and 2H and -CH2O-), 7.4 (d, 2H, Ar-H, J= 8Hz), 7.8 (d, 2H, Ar-H, J= 8Hz)
After ketal-izing example of reference 7 benzoylacetic-acid ethyl ester by ethylene KURIKO-RU, it returned with lithium hydride aluminum and considered as the 3-phenyl -3 and 3-ethylene dioxy propanol -1. p-tosyl chloride was made to react to this under existence of triethylamine, and the crystalline 1-(p-toluenesulfonyloxy)-3-phenyl -3 and 3-ethylene dioxy propane were obtained with about 70% of yield.
Colorless oily matter m.p.48-50 degree-CIR (KBr) 2892, 1597, and 1354, 1178cm~1, 1 H-NMR delta= 2.27 (t, 2H, -CH2CH2OTs, J= 8Hz) (90MHz, CDCl3), 2.44 (s, 3H, Ar-CH3) and 3.6- 4.1 (m, 4H, and -OCH2CH2O-), 4.15 (t, 2H, -CH2CH2OTs, J= 8Hz), and 7.2- 7.5 (m, 7H, Ar-H) and 7.76 (d, 2H, Ar-H, J= 8Hz)
[0047] The 4-% of the weight cyclohexane solution of example 1 Pori (p-(tert-buthoxycarbonyloxy) styrene) was prepared, and the diphenyl (p-phenylthiophenyl) sulfonium hexafluoroantimonate which is 5% of the weight (it is two-mol % to a monomeric unit) of a photo-oxide generating agent was dissolved to this polymer. Addition of the 2-methyl-2-(p-toluenesulfonyloxy)-3-keto butanoic acid tert butyl ester which is the acid growth agent obtained in the example 1 of reference in this solution was carried out to this polymer 10% of the weight (it is six-mol % to a monomeric unit). It considered as the thin film which carries out spin spreading of this solution on a silicon wafer, and has 0.5-micrometer thickness, and prebake processing was performed for this for 1 minute at 100 degrees C. For the comparison, the poly membrane which does not contain an acid growth agent was prepared similarly. These poly membranes were drawn for 7 minutes, and after changing time amount and carrying out UV irradiation of each, postbake processing was performed at 100 degrees C. Since the acid decomposed and thickness reduced this macromolecule, thickness change was measured and the sensitization rate was evaluated. To the acidolysis of a macromolecule being completed by exposure for 17 seconds, when an acid magnification agent is added, in the acid growth agent additive-free case, in order for the reduction in thickness to be about 25% and to dissolve completely in the exposure for 17 seconds, the exposure for 50 seconds was required by the postbake for 2 minutes. Moreover, when an acid growth agent was added, reduction of the thickness in postbake has taken place rapidly, and the magnification effectiveness was accepted clearly. Image formation was checked by carrying out postbake processing behind the bottom of exposure through a mask.
[0048] Instead of the diphenyl (p-phenylthiophenyl) sulfonium hexafluoroantimonate used as a photo-oxide generating agent in example 2 example 1, 6% of the weight of 2 and a 3-diphenyl-3-

keto-2-hydroxy-1-(p-toluenesulfonyloxy) propane were added as a photo-oxide generating agent, and the addition effectiveness of the 2-methyl-2-(p-toluenesulfonyloxy)-3-keto butanoic acid tert butyl ester obtained in the example 1 of reference was investigated. After carrying out spin spreading of the thin film on a silicon wafer like an example 1, postbake was performed at 100 degrees C for 3 minutes after carrying out ultraviolet-rays exposure. In the acid growth agent additive-free case, although reduction of the thickness containing an acid growth agent was rapidly completed by the exposure for 60 seconds, by the same exposure time, thickness decreased only about 15%, but in order to complete thickness reduction, it required the exposure time for 180 seconds.
3.4% of the weight of triphenylsulfonium triflate and the 2-methyl-2-(p-toluenesulfonyloxy)-3-keto butanoic acid tert butyl ester which is 1% of the weight of an acid growth agent were added to the cyclohexane solution of a polymer used in the example 3 example 1 to the polymer, and the thin film was prepared. After exposing ultraviolet rays, when postbake was performed at 100 degrees C for 3 minutes, the reduction in thickness was completed by the exposure for 55 seconds. In order in an additive-free case to remain in reduction of about 15% of thickness and to complete an acid growth agent by the same exposure time, the exposure time for 150 seconds was required.
[0049] 10% of the weight of diphenyl (p-phenylthiophenyl) sulfonium hexafluoroantimonate and the cis--1-methyl-1-hydroxy-2-(p-toluenesulfonyloxy) hexane obtained in the example 5 of reference were added to the cyclohexane solution of a polymer used in the example 4 example 1 5% of the weight to the polymer, and on the silicon wafer, spin spreading was carried out and it considered as the 0.5-micrometer thin film. After performing postbake for 2 minutes at 100 degrees C after exposing ultraviolet rays, negatives were developed by ethanol, and the residual membrane was measured. Although all film dissolved by the exposure time for 10 seconds when an acid growth agent was added, the exposure time for 70 seconds or more was required of additive-free.
The 1 and 2-epoxy-2-methyl-3-hydroxy propane compounded in the example 6 of reference instead of the cis--1-methyl-1-hydroxy-2-(p-toluenesulfonyloxy) hexane used in example 5 example 4 was added. When UV irradiation, postbake processing, and ethanol development were performed similarly, the exposure time required in order to dissolve all film by adding an acid growth agent was able to be shortened to the quadrant.
[0050] 10% of the weight of diphenyl (p-phenylthiophenyl) sulfonium hexafluoroantimonate and the cis--1-methyl-1-hydroxy-2-(p-toluenesulfonyloxy) hexane obtained in the example 5 of reference were added to 2:1 copolymers (Mw=4.01x104, Mw/Mn=1.74) of example 6 methyl methacrylate and methacrylic-acid 2-phenyl-2-propyl ester 5% of the weight, and on the silicon wafer, spin spreading was carried out and it considered as the 0.23-micrometer thin film. After irradiating ultraviolet rays at this, postbake processing was performed for 2 minutes at 100 degrees C, negatives were developed by ethanol, and the remaining rate of membrane was measured. By adding an acid growth agent, the exposure time required for becoming residual membrane zero was able to be shortened to the quadrant.
Same exposure, postbake, and ethanol development were performed using the 1-(p-toluenesulfonyloxy)-3-phenyl -3 and 3-ethylene dioxy propane which were compounded in the example 7 of reference instead of the cis--1-methyl-1-hydroxy-2-(p-toluenesulfonyloxy) hexane used in example 7 example 6. By adding this acid growth agent, the exposure time for solubilizing all film was able to be shortened to about 1/3.
[0051] In the cyclohexanone solution of a polymer used in the example 8 example 1, the diphenyl (p-phenylthiophenyl) sulfonium hexafluoroantimonate which is a photo-oxide generating agent, and the 1-(p-toluenesulfonyloxy)-3-phenyl -3 and 3-ethylene dioxy propane were added 10% of the weight to the polymer, respectively, and on the silicon wafer of three sheets, spin spreading was carried out, respectively and it considered as the 0.25-micrometer thin film. After irradiating ultraviolet rays through the fenestera rotunda with a diameter of 3mm at these thin films, it heat-treated at 105 degrees C, 115 degrees C, and 125 degrees C. After the discoloration accompanying reduction in thickness appeared immediately as a round shape which is 3mm, the round shape increased with time amount. Postbake time amount until a diameter is set to 12mm

was 30 seconds by 125 degrees C for 45 seconds at 115 degrees C in 105 degrees C for 7 minutes. This is because the acid generated with light is spread with heating within a poly membrane and acid generating by decomposition of an acid growth agent is caused one after another in connection with it. When an acid growth agent was not added, such reduction did not take place.

[0052] % of the 15-mol 1-(p-toluenesulfonyloxy)-3-phenyl -3 as two-mol % 2, and the 3-diphenyl-3-keto-2-hydroxy-1-(p-TORUHEN sulfonyloxy) propane and the acid growth agent as a photo-oxide generating agent and 3-ethylene dioxy propane were added to the solution of 2-methoxy ethyl acetate of an example 9p-trimethylsilyloxy styrene homopolymer (5.35x104, Mw/Mn=1.69). After carrying out spin spreading of this solution by 1000rpm on the silicon wafer and carrying out prebake for 30 seconds at 100 degrees C, time amount was changed, ultraviolet rays were irradiated and postbake was given for 30 seconds at 100 degrees C. When it was immersed for 10 seconds into ethanol and negatives were developed, the exposure time which a poly membrane solubilizes completely was shortened to about 1/3 compared with acid growth agent additive-free.

After adding 3% of the weight of diphenyl (p-phenylthiophenyl) sulfonium hexafluoroantimonate, and 3% of the weight of 2-methyl-2-(p-toluenesulfonyloxy)-3-keto butanoic acid tert butyl ester to the cyclohexane solution of 1:1 copolymers (Mw=5.15x104, Mw/Mn=2.04) of example 10 methyl methacrylate and glycidyl methacrylate to this polymer, spin spreading was carried out on the anodized aluminum plate. To this, time amount was changed, ultraviolet rays were exposed, and after carrying out postbake at 100 degrees C for 3 minutes, the plate was washed with toluene. When compared with the case where an acid growth agent is not added, the exposure time which insolubilization of a copolymer takes was shortened to 1/5.

[0053] Addition of the 2-methyl-2-(p-toluenesulfonyloxy)-3-keto butanoic acid tert butyl ester which is the acid growth agent obtained in the example 1 of reference in the cyclohexane solution of a polymer used in the example 11 example 1 was carried out to this polymer 10% of the weight (it is six-mol % to a monomeric unit). It considered as the thin film which carries out spin spreading of this solution on a silicon wafer, and has 0.27-micrometer thickness, and prebake processing was performed for this for 1 minute at 100 degrees C. For the comparison, the poly membrane which does not contain an acid growth agent was prepared similarly. 3.5% of the weight of triphenylsulfonium TORIFURA-TO was dissolved in the 0.07-% of the weight isopropyl alcohol solution of novolak resin to resin, and spin spreading was carried out on the poly membrane which prepared this previously. Prebaking for 1 minute at 100 degrees C, the film which consists of two-layer [of the film containing a photo-oxide generating agent and the film containing an acid growth agent] became the thickness of 0.62 micrometers as a whole. After exposing ultraviolet rays on this two-layer film, postbake processing was performed at 100 degrees C, and negatives were developed in 40-degree C ethanol for 1 minute. When asked for the relation between the exposure time and a remaining rate of membrane, having high-sensitivity-ized the two-layer film which added the acid growth agent 20 times compared with the additive-free two-layer film was admitted.

[0054] In example 12 example 11, when the completely same exposure as an example 10 was performed about the film of the two-layer structure which added triphenylsulfonium hexafluoroantimonate instead of triphenylsulfonium TORIFURA-TO as a photo-oxide generating agent, 18 times as many high sensitivity-ization as this was accepted by addition of an acid growth agent.

The sensibility of the film of the two-layer structure which added the triphenylsulfonium hexafluoroantimonate prepared in the example 13 example 11, and the film which added triphenylsulfonium hexafluoroantimonate to the polymer of the example 1 which is a well-known chemistry magnification mold photoresist was measured. Consequently, the film of the two-layer structured type which separates and contains an acid growth agent showed 25 times as many high sensitivity as this to the chemistry magnification resist.

[Translation done.]